MS13-1-9 In situ and ex situ electron diffraction revealing diverse structural transformations of $La_xSr_{2-x}MnO_{4-\delta}$ upon gas reduction
#MS13-1-9

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Abstract
Stability under reducing working atmospheres is an important quality in electrode materials for solid oxide fuel cells. For Ruddlesden-Popper manganites $La_xSr_{2-x}MnO_{4-\delta}$ with $0.25 \leq x \leq 0.6$, this structure preservation has been demonstrated by in situ high-temperature neutron and X-ray powder diffraction. [1] However, in situ and ex situ 3D electron diffraction now reveal that $La_{0.5}Sr_{1.5}MnO_4$ nevertheless undergoes unexpected structure transformations upon heating in a reducing atmosphere such as diluted hydrogen gas.While previously unobserved, the extra reflections disclosing these transformations can be easily picked up by electron diffraction. This is because the interaction of matter with electrons is more than one million times stronger than with X-rays or neutrons, which makes them more suitable to elucidate subtle transitions. Electron diffraction allows to obtain two-dimensional single-crystal diffraction patterns for submicron sized crystals, of which X-ray and neutron diffraction can only produce one-dimensional powder data that contain less information.Using a dedicated environmental holder, 3D electron diffraction shows that $La_{0.5}Sr_{1.5}MnO_4$ partially transforms from its pristine K_2NiF_4-type symmetry to a perovskite phase, when it is heated inside the transmission electron microscope in diluted hydrogen. When the material is annealed ex situ in diluted H_2/Ar, the same phenomenon is detected for a part of the crystals, while other crystals show the occurrence of a superstructure accompanying oxygen-vacancy order. This oxygen-vacancy order was not observed in any of the in situ experiments.Similarly, in situ and ex situ 3D electron diffraction show different structural behaviour for the gas reduction of Sr_2MnO_4 when this happens inside or outside the electron microscope: Sr_2MnO_4 transforms to the monoclinic $P2_1/c$ supercell known in literature [2] when reduced ex situ, but maintains the tetragonal symmetry when reduced in situ. On the other hand, $LaSrMnO_4$ and $La_{0.25}Sr_{1.75}MnO_4$ indeed show no differences in their space groups upon reduction. In-depth study of the diverging reduction behaviour inside and outside the microscope could offer new insights on the degradation of real life working electrodes, and help to optimize their performance life time.

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References
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